3. RESULTS

Results for the work discussed in Section 2 are presented in this section. Groundwater data are included in Appendix D (on the attached CD-ROM). Section 3.1 discusses the results from ISB performance monitoring. Sections 3.2 and 3.3 present the results of in situ geochemical and water level monitoring, respectively. Results from the radiological analyses are presented in Section 3.4. Quality assurance (QA) results are summarized in Section 3.5 and results of the microcosm studies are reported in Section 3.6.

3.1 Performance Monitoring Data

This section presents results of groundwater monitoring in the context of overall ISB performance. During this reporting period, extensive groundwater monitoring was conducted to evaluate the effectiveness of two different injection strategies. Section 3.1.1 describes the technical approach to evaluating ISB performance at this stage. Sections 3.1.2 and 3.1.3 present results related to electron donor distribution and utilization. Section 3.1.4 presents data pertaining to geochemical conditions at each monitoring location, and Section 3.1.5 presents data related to establishment of ARD conditions. Section 3.1.6 specifically discusses trans-DCE data.

3.1.1 Technical Approach

The performance monitoring strategy during this phase of operations was to describe the distribution of electron donor in terms of COD data (presented in Section 3.1.2), and to evaluate the importance of differing fermentation pathways by examining the relative molar concentrations of propionate, acetate, and butyrate at locations within the treatment cell (presented in Section 3.1.3).

As described in Section 2.1, two different injection strategies were used during the reporting period in an attempt to achieve the desired distribution of electron donor throughout the residual source area. The volume (1X or 4X), the nominal concentration of the sodium lactate (3 or 6%), and the date(s) of injection identify the specific injections. For each injection, spatial trends are reported by dividing the wells within the treatment cell into four groups. Wells TSF-05A, TSF-05B, TAN-25, TAN-31, and TAN-1859 are referred to as source area wells because they are located within 100 ft of TSF-05 in the zone of residual contamination and are also within the impacted zone of electron donor injections at TSF-05. Wells TAN-26 and TAN-37C are referred to as deep wells, as they are screened at depths greater than 300 ft and are generally characterized by extremely reducing conditions and low contaminant concentrations. Wells TAN-37A, TAN-37B, TAN-1860, TAN-1861, TAN-28, and TAN-30A are referred to as downgradient wells and are located between 125 and 300 ft downgradient from TSF-05, outside the area of residual contamination and electron donor injection influence from TSF-05. Wells TAN-D2, TAN-29, TAN-27, and TAN-10A are referred to as outside wells because they are located along the perimeter of the treatment cell greater than 300 ft downgradient, or 100 ft cross- or up-gradient, from TSF-05 and are also generally outside the zone of influence of electron donor injections at TSF-05.

An understanding of the basis from which technical decisions have been made is necessary before a detailed description of ISB performance can take place. One of the important drivers in a system actively undergoing ARD is the hydrogen (H_2) that is produced from fermentation of injected electron donor. Hydrogen is the electron donor used by *Dehalococcoides ethenogenes*, the only isolated bacterium capable of complete ARD of TCE to ethene (Maymo-Gatell 1997). A strain of this bacterium has been detected at TAN using DNA sequencing (Wood, Cummings, and Sorenson 2002) and is likely the bacterium responsible for complete dechlorination of TCE to ethene at TAN.

Figure 3-1 illustrates the hydrogen production process by the microbial degradation of lactate and its associated fermentation products. Lactate fermentation is thought to occur via two primary pathways. The first is referred to as the acetate pathway whereby lactate (CH_3CH_2OCOO) will degrade to acetate (CH_3COO^-), carbonate, and free hydrogen (Equation 3-1). The second pathway is referred to as the propionate pathway whereby lactate (CH_3CH_2OCOO) degrades to propionate (CH_3CH_2COO), acetate (CH_3COO^-), and carbonate (Equation 3-2).

$$\text{lactate}^- + 2H_2O \rightarrow \text{acetate}^- + HCO_3^- + 2H_2 + H^+ . \quad (3\text{-}1)$$

$$\text{lactate}^- \rightarrow \text{propionate}^- + \text{acetate}^- + HCO_3^- + H^+ . \quad (3\text{-}2)$$

The different biochemical pathways, however, may not be equally efficient in promoting extent and/or rate of ARD, which has significant implications regarding ARD performance. The fermentation of lactate via the acetate pathway (Equation 3-1) occurs rapidly, and thus generates higher levels of hydrogen more rapidly than other fermentation pathways. The propionate pathway (Equation 3-2) produces propionate and acetate at a stoichiometric ratio of 2:1 and does not directly produce free hydrogen. The propionate generated via reaction Equation 3-2 is, in turn, fermented to acetate, carbonate, and free hydrogen through the following reaction:

$$\text{propionate}^- + 3H_2O \rightarrow \text{acetate}^- + HCO_3^- + 3H_2 + H^+ . \quad (3\text{-}3)$$

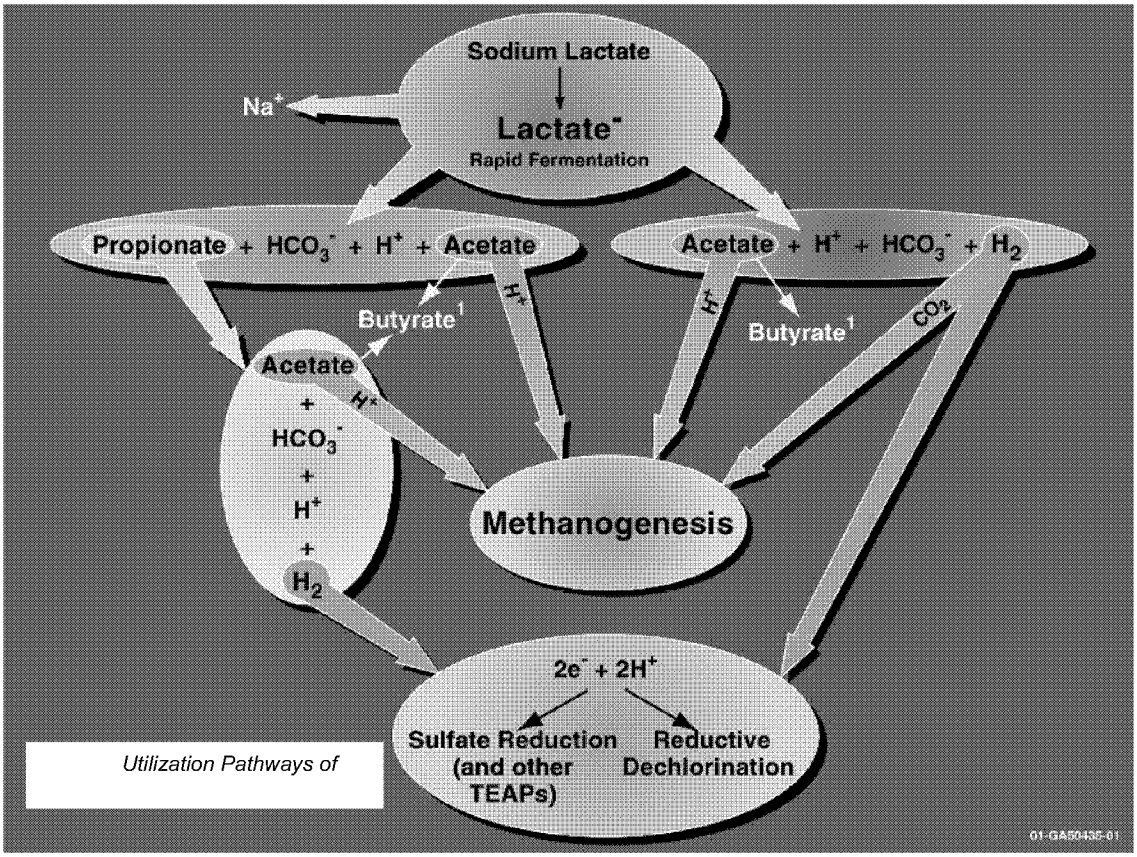

Figure 3-1. Microbial utilization pathways of lactate and its fermentation products.

Under extremely reducing conditions, the acetate is further oxidized to carbonate and hydrogen, via Equation 3-4:

$$\text{acetate}^- + 4H_2O \rightarrow 2HCO_3 + 4H_2 + H^+ . \quad (3\text{-}4)$$

Fermentation of lactate primarily by propionate oxidation is a much slower process than the acetate dominant pathway because the reaction is self-limiting by the partial pressure of hydrogen (He et al. 2002). Therefore, this pathway provides relatively low levels of free hydrogen sustained over much longer periods of time. Published research has suggested that complete dechlorination to ethene is more efficient in terms of electron donor utilization under such conditions where the electron donor used provides a slow release of hydrogen (Fennell, Gossett, and Zinder 1997). The rationale is that hydrogen-utilizing competitors to dechlorinators (i.e., hydrogenotrophic methanogens) require much higher hydrogen partial pressures and so by limiting hydrogen to low partial pressures, dechlorinators are favored. Therefore, at TAN, the most efficient ARD is believed to occur when lactate fermentation occurs (via the propionate pathway [Equation 3-2]) and propionate, and subsequently acetate, are the dominant hydrogen-producing processes (Equations 3-3 and 3-4). In order to increase ARD efficiency at TAN, the lactate injection strategy has been focused on maximizing the amount of time during which propionate and acetate are the primary electron donors.

Another potential electron donor that has been observed at TAN, although not in concentrations high enough to significantly affect ARD, is butyrate. The generation of butyrate under the geochemical conditions present at TAN, however, is not well understood. A hypothetical pathway for butyrate production is shown in the following reaction (Equation 3-5):

$$2\ \text{acetate}^- + H^+ + 2H_2 \leftrightarrow \text{butyrate}^- + 2H_2O . \quad (3\text{-}5)$$

Butyrate is generated when electron donor and H^+ concentrations are sufficiently high, as occurs in the area nearest the sodium lactate injection point at TAN. As butyrate is transported downgradient, it can be fermented to acetate and hydrogen, which can stimulate both methanogenesis and ARD.

3.1.2 Electron Donor Distribution

This section describes the different injection strategies, correlates the amount of electron donor that was distributed to each of the respective well groups, and provides tables of pertinent data to show the impact of each injection strategy on the electron donor distribution at the various locations within the treatment cell. It should be noted that the molar percentages may not sum to 100% because butyrate is not included in these tables. Chemical oxygen demand concentrations and electron donor molar concentrations in the source area wells are presented in Figures 3-2 through 3-10.

The first of the two injection strategies employed during this reporting period was the 4X 3% injection strategy. These injections, which were performed on November 19, 2002, January 6, 2003, February 26, 2003, April 9, 2003, and June 2, 2003, consisted of approximately 48,000 gal of a 3% nominal concentration of sodium lactate injected into TSF-05. Each injection was completed in 2 to 3 days. The larger volume was used with the objective of increasing the radial distribution of electron donor, particularly to the downgradient portions of the aquifer in the TAN-37 area. The 3% solution was used to minimize vertical transport of electron donor to the deeper portions of the aquifer, as measured at TAN-26 and TAN-37C. The second injection strategy was the 1X 6% injection strategy (approximately 12,000 gal, 6% nominal sodium lactate concentration), which was performed on July 21, 2003, and September 8, 2003. The 1X 6% injection strategy was designed to reduce the volume of aerobic water introduced into the ISB treatment cell.

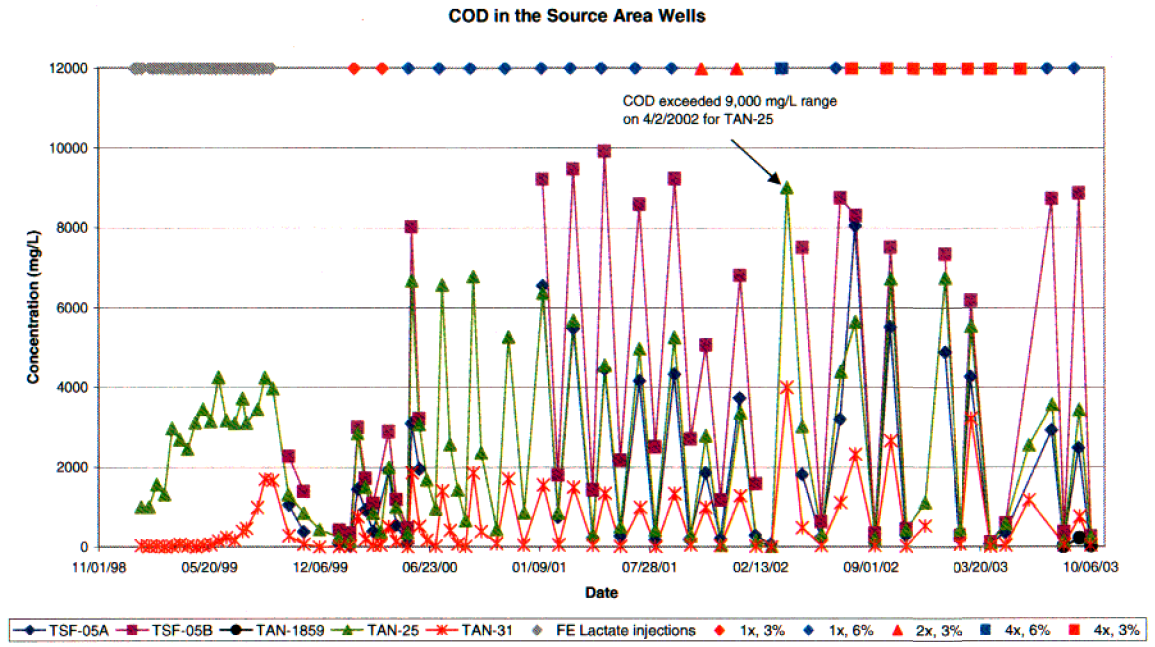

Figure 3-2. Source area wells chemical oxygen demand.

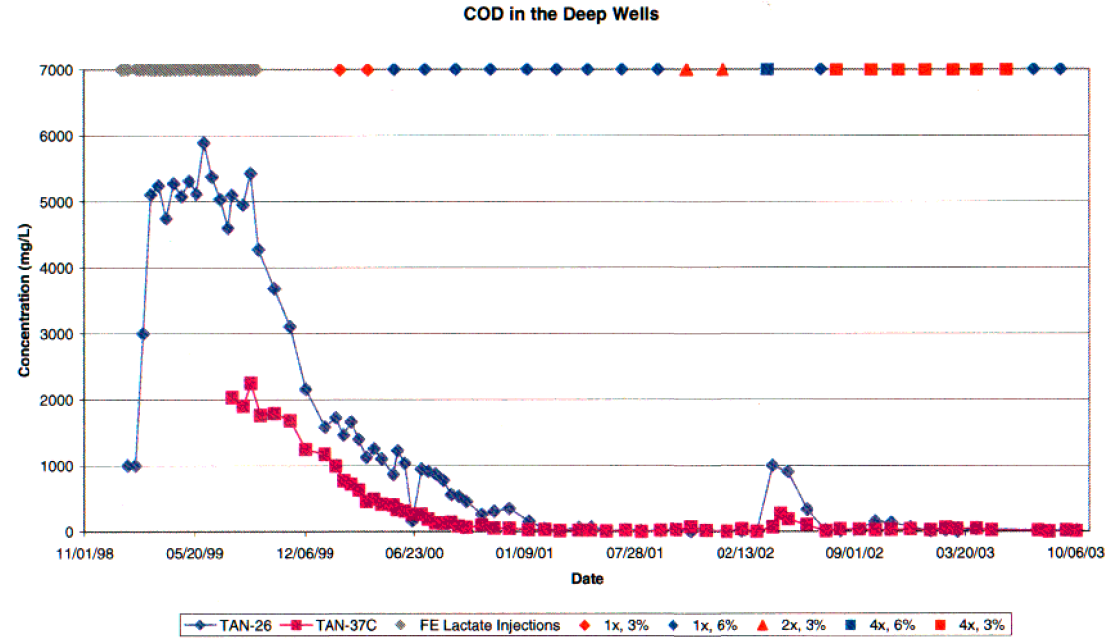

Figure 3-3. Deep wells chemical oxygen demand.

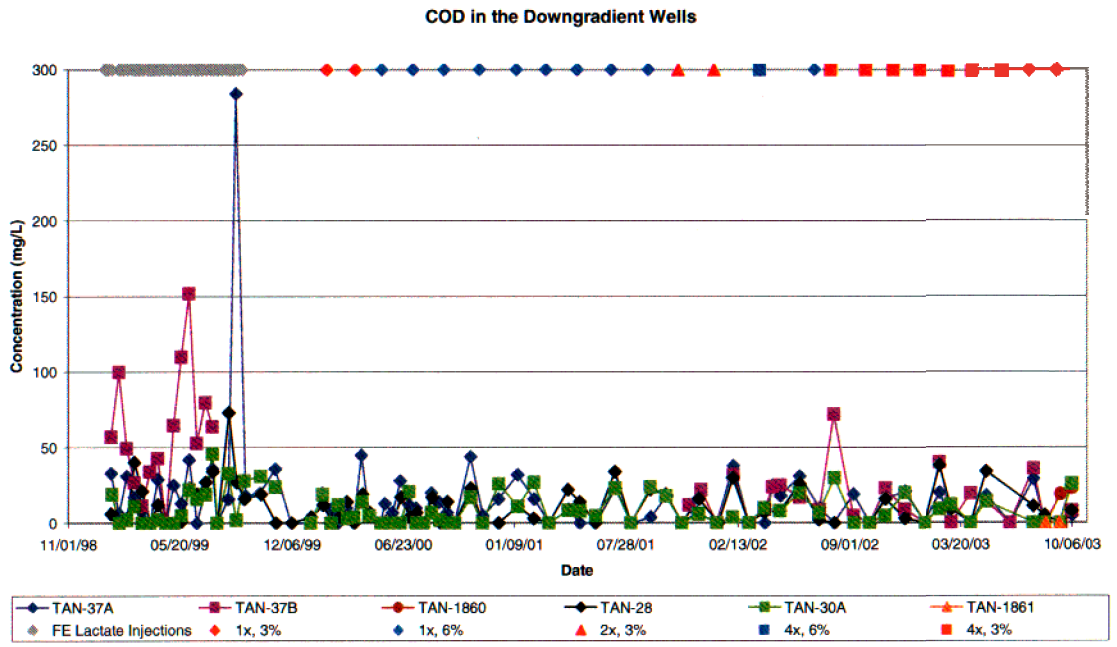

Figure 3-4. Downgradient wells chemical oxygen demand.

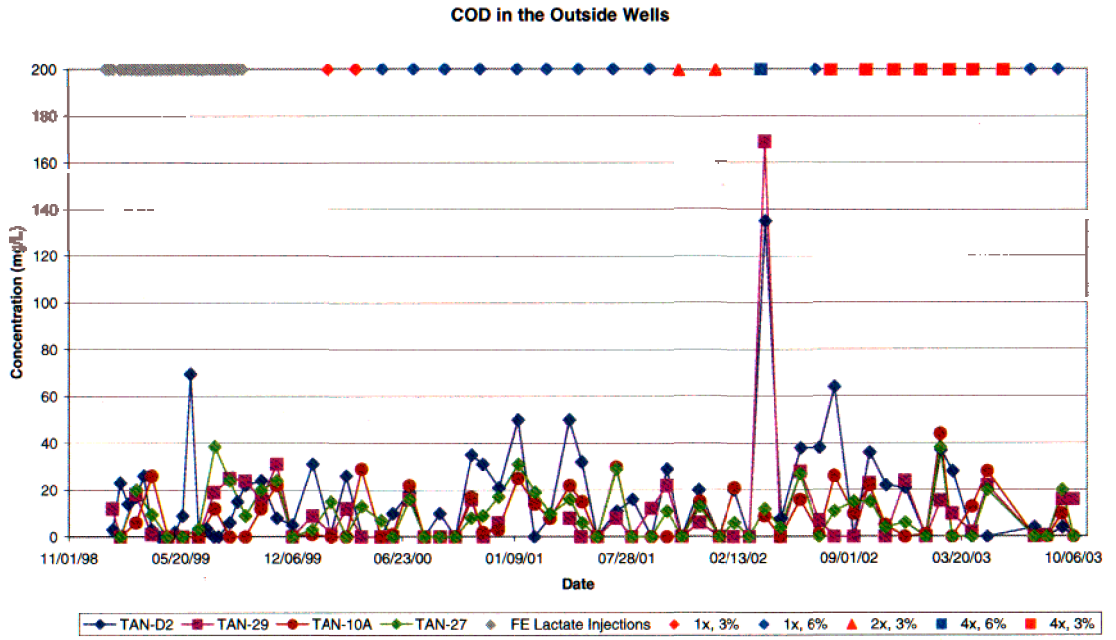

Figure 3-5. Outside wells chemical oxygen demand.

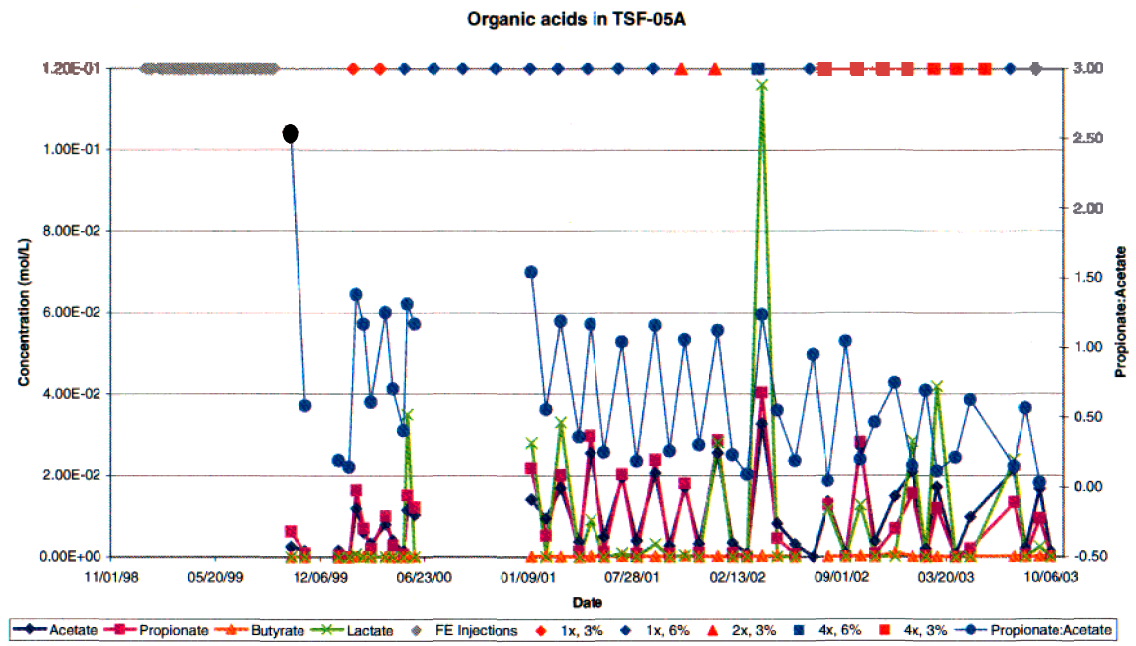

Figure 3-6. Organic acids at TSF-05A.

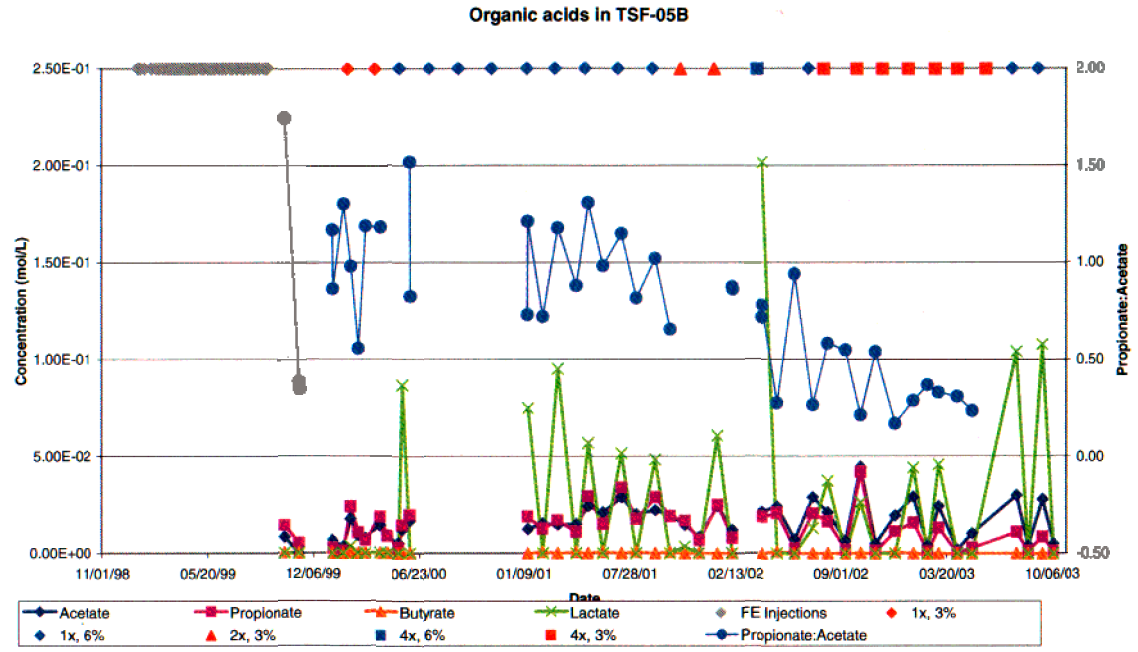

Figure 3 Organic acids at TSF-05B.

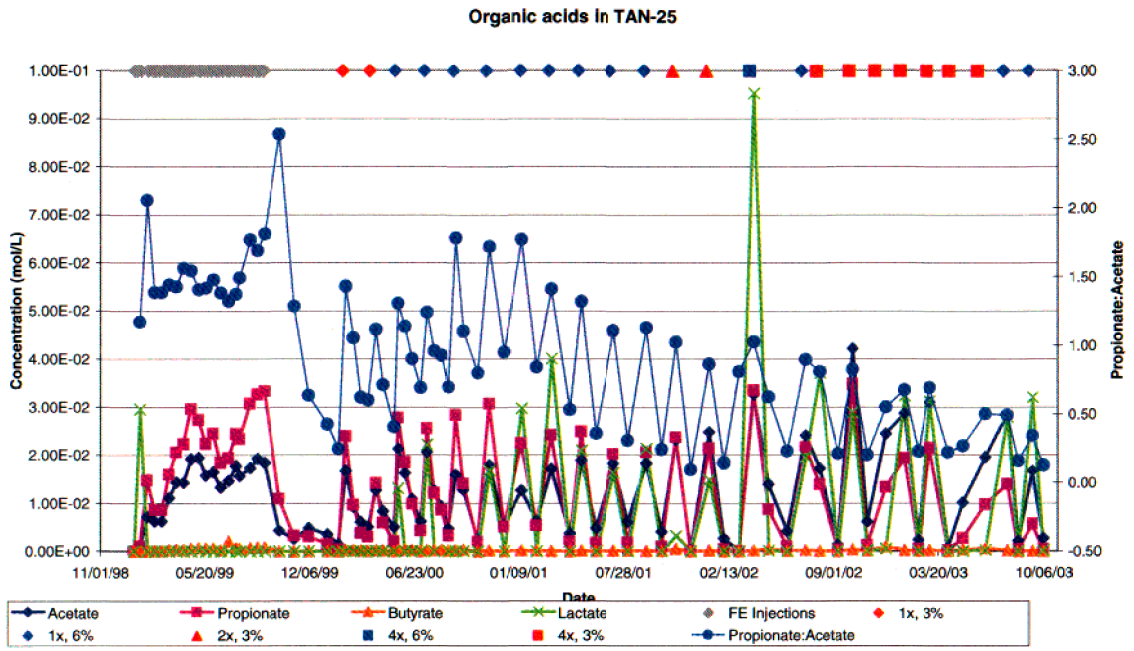

Figure 3-8. Organic acids at TAN-25.

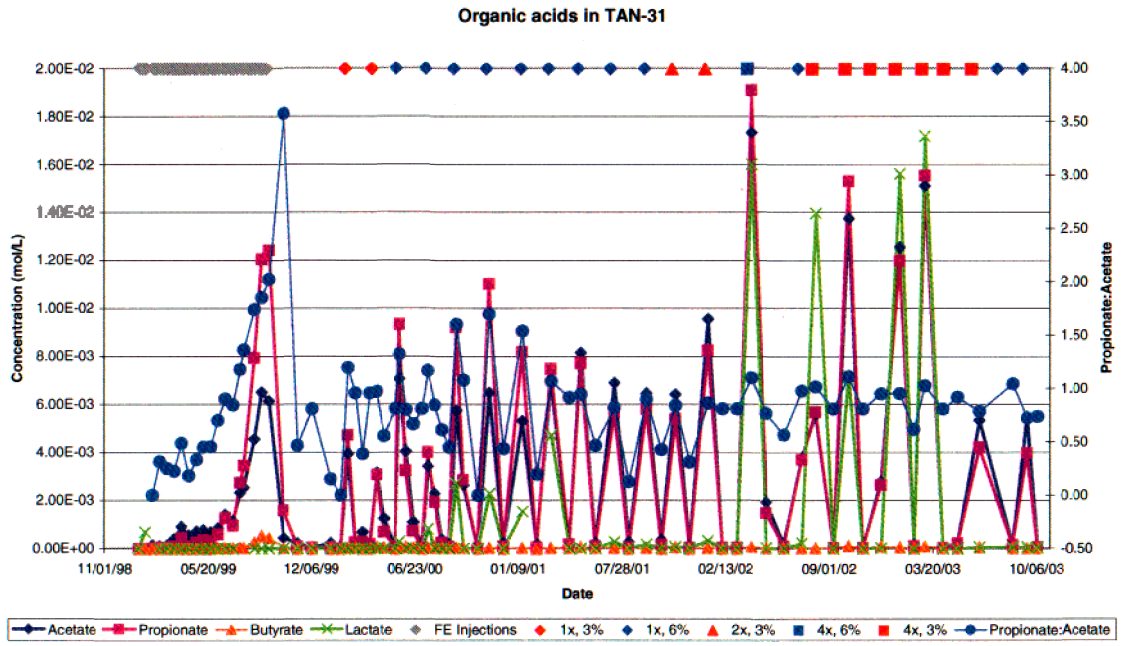

Figure 3-9. Organic acids at TAN-31.

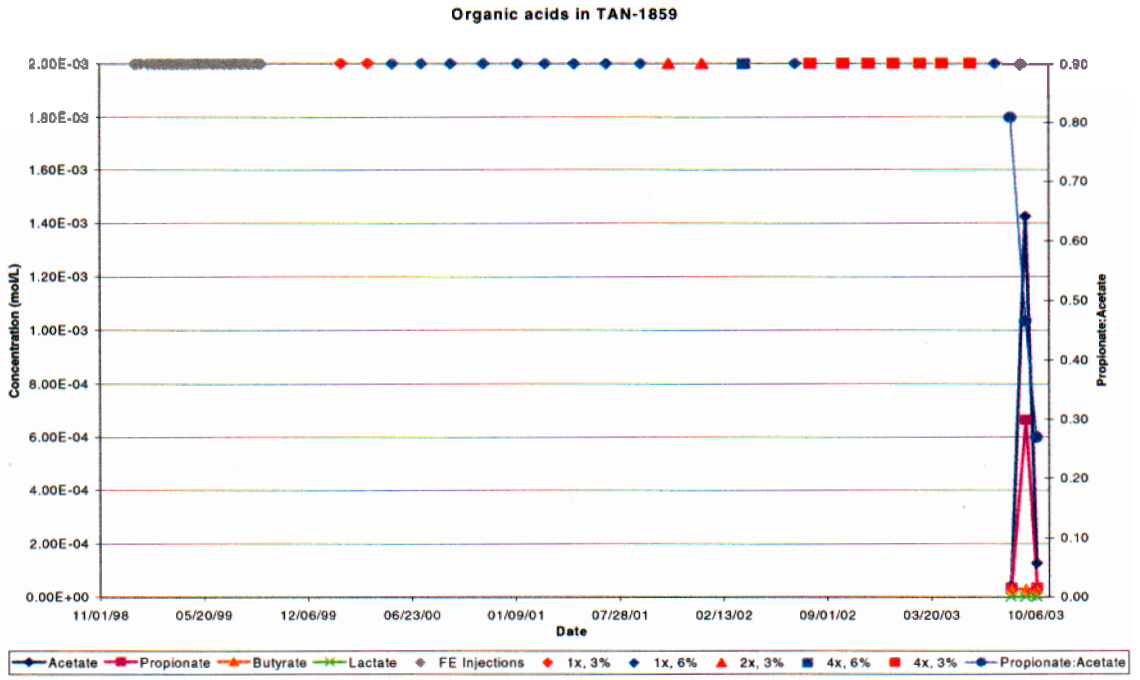

Figure 3-10. Organic acids at TAN-1859.

3.1.2.1 Source Area Wells. Tables 3-1 through 3-5 summarize the electron donor data collected following each 4X 3% injection in all of the source area wells. Electron donor was distributed in high concentrations to all of the source area wells. The highest COD concentrations were observed in TSF-05B (COD at ~7,000 mg/L), followed by TAN-25 (COD at ~6,000 mg/L), TSF-05A (~4,500 mg/L), and TAN-31 (~3,000 mg/L), approximately 1 week after the 4X 3% injections. Tables 3-6 and 3-7 summarize the electron donor data collected following each 1X 6% injection. Higher concentrations of COD (~8,800 mg/L) were observed at TSF-05B than were observed during the 4X 3% injection, but lower concentrations were observed at TAN-25 (~3,500 mg/L), TSF-05A (~2,700 mg/L), and TAN-31 (1,000 mg/L) as compared with the 4X 3% injection. The 1X 6% injections resulted in higher concentrations of lactate near the injection point but less distribution to downgradient and crossgradient locations.

Table 3-1. Electron donor data for 4X 3% injection on November 19, 2002.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate: Acetate (molar)
TSF-05A	23	531	<0.223 0	501.6 30	875.8 65	N/A
TSF-05B	23	N/A	<0.223 0	836.5 36	1,161.0 62	N/A
TAN-25	21	1,100	43.8 1	979.9 34	1,443.9 62	0.55
TAN-31	21	531	2.50 1	194.8 48	165.5 50	0.95

Table 3-2. Electron donor data for 4X 3% injection on January 6, 2003.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate: Acetate (molar)
TSF-05A	9	4,878	2,534.5 44	1,141.7 24	1,239.4 32	0.74
TSF-05A	35	213	<0.223 0	21.2 23	113.1 36	N/A
TSF-05B	9	7,344	3,945.8 49	1,168.3 18	1,724.7 33	0.55
TSF-05B	35	285	<0.223 0	62.6 18	236.2 82	N/A
TAN-25	9	6,750	2,879.2 40	1,417.4 24	1,695.5 36	0.68
TAN-25	35	439	<0.223 0	39.1 18	139.5 78	N/A
TAN-31	9	N/A	1,391.1 39	877.1 30	742.7 31	0.95
TAN-31	35	67	<0.223 0	8.5 35	11.1 56	N/A

Table 3-3. Electron donor data for 4X 3% injection on February 26, 2003.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
TSF-05A	5	4,266	3,735.7 59	873.8 17	1,017.7 24	0.69
TSF-05A	42	72	<0.223 0	4.8 10	33.9 86	N/A
TSF-05B	6	6,174	4,089.2 55	965.5 16	1,451.4 29	0.54
TSF-05B	42	114	<0.223 0	24.6 14	116.9 84	N/A
TAN-25	6	5,531	2,778.6 37	1,568.3 26	1,832.0 37	0.69
TAN-25	42	87	<0.223 0	12.6 17	46.5 80	N/A
TAN-31	6	N/A	1,391.1 36	877.1 32	742.7 32	1.03
TAN-31	42	19	<0.223 N/A	<5.0 N/A	<5.0 N/A	N/A

Table 3-4. Electron donor data for 4X 3% injection on April 9, 2003.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
TSF-05A	27	348	<0.223 0	153.4 17	584.3 81	N/A
TSF-05B	28	597	<0.223 0	218.8 22	613.4 77	N/A
TAN-25	28	578	<0.223 0	197.4	601.4	N/A
TAN-31	28	42	<0.223 0	16.5 45	14.5 49	N/A

Table 3-5. Electron donor data for 4X 3% injection on June 2, 2003.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
TSF-05A	This location not sampled					
TSF-05B	This location not sampled					
TAN-25	15	2,547	19.2 1	714.1 32	1,153.9 65	0.50
TAN-31	15	1,179	5.51 1	308.7 44	316.6 55	0.79

Table 3-6. Electron donor data for 1X 6% injection on July 21, 2003.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
TSF-05A	7	2,925	2,124.7 40	983.4 23	1,268.8 36	0.63
TSF-05A	35	81	<0.223 0	23.1 13	125.4 86	N/A
TSF-05B	8	8,730	9,275.2 72	811.5 8	1,778.2 21	0.37
TSF-05B	35	377	<0.223 0	96.2 25	235.4 75	N/A
TAN-25	8	3,564	2,492.3 40	1,023.6 20	1,684.2 40	0.49
TAN-25	35	139	<0.223 0	25.6 13	131.585	N/A
TAN-31	This location not sampled					
TAN-31	35	49	6.476 18	11.4 38	8.8 37	N/A

Table 3-7. Electron donor data for 1X 6% injection on September 8, 2003.

Well	Time Elapsed After Injection (days)	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
TSF-05A	7	2,475	217.9 9	688.2 33	983.0 58	0.57
TSF-05A	28	71	<0.223 N/A	<5.0 N/A	67.7 N/A	N/A
TSF-05B	8	8,865	9,602.8 74	636.9 6	1,661.5 19	0.31
TSF-05B	28	260	<0.223 0	87.5 19	298.7 80	N/A
TAN-25	8	3,429	2,852.9 59	417.4 10	988.7 31	0.34
TAN-25	28	236	9.143 3	24.9 11	160 85	N/A
TAN-31	9	758	5.390 1	291.5 42	325.1 57	0.72
TAN-31	28	37	3.438 17	4.85 30	5.3 40	N/A
TAN-1859	9	214	<0.223 0	48.5 31	84.2 67	N/A
TAN-1859	28	15	<0.223 N/A	<5.0 N/A	7.5 N/A	N/A

3.1.2.2 Downgradient, Outside, and Deep Wells. No COD was observed in the deep wells and very little (<60 mg/L) was observed in the downgradient and outside wells. Therefore, little distinction could be made between the different injection strategies using these data, as little or no electron donor reached these locations.

3.1.3 Electron Donor Utilization

The optimization process involves not only distribution of donor (as discussed above) but also includes monitoring of the amendment utilization rate in relation to the dechlorination rate. The goal of this process is to minimize injection frequency while maintaining a relatively high rate of dechlorination. Concentrations of electron donor within the residual source area were determined by measuring COD, lactate, and reaction products propionate, acetate, and butyrate. Concentration changes for these parameters following each injection event provide information related to electron donor utilization rate and pathway. As illustrated in Figure 3-11, COD concentrations drop quickly over an approximately 1-month period following each injection. (COD is used as a surrogate for the combined electron donor constituents, as it represents lactate and the rapidly produced fermentation products.)

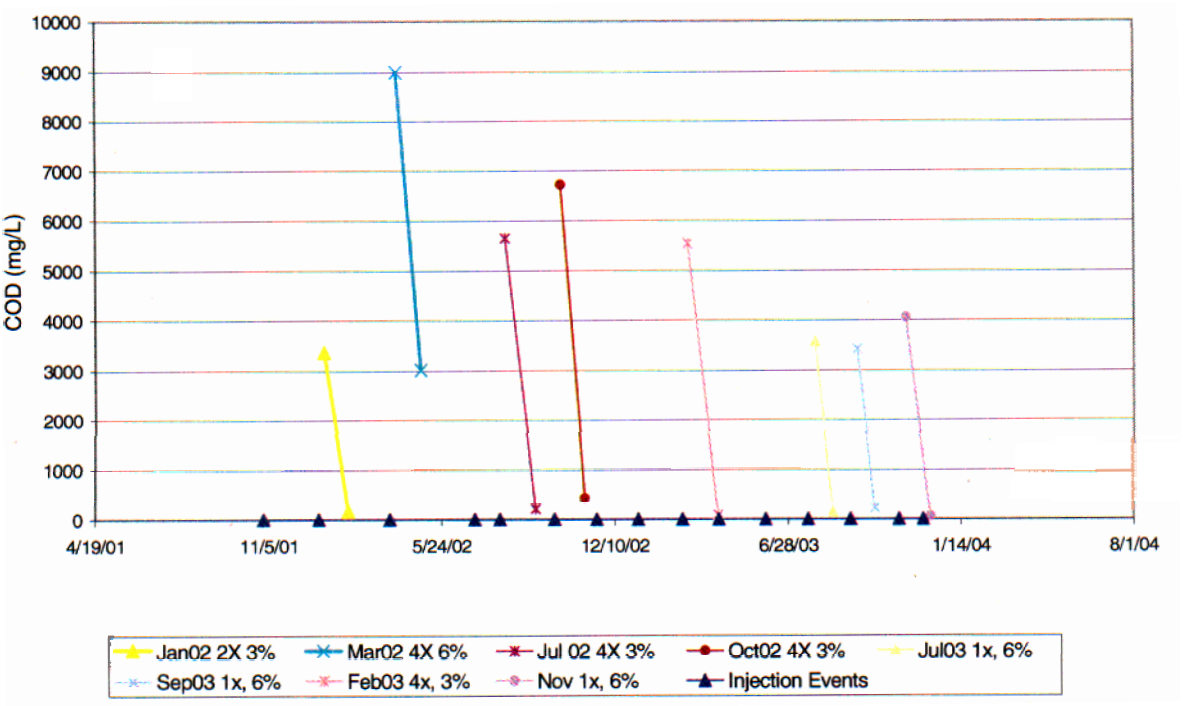

Figure 3-11. Example of chemical oxygen demand concentration drops at TAN-25 following injection events.

The effects of the different injections on electron donor utilization, as indicated by changes in the first order utilization rates of COD and lactate, are presented for source area wells TSF-05A, TSF-05B, TAN-25, and TAN-31. There were not sufficient electron donor concentrations in the deep, downgradient, or outside wells to calculate utilization rates. On several occasions, only one sampling event was conducted between injections. In these cases, degradation rates could not be analyzed.

The first order rate law for the consumption of reactant A is:

$$\frac{-d[A]}{dt} = k[A] \qquad (3\text{-}6)$$

where:

$[A]$ = concentration of A

t = time

k = fraction of A consumed per unit of time (rate constant).

Integration of Equation 3-6 with respect to time leads to:

$$[A]=[A]_0 e^{-kt} \quad (3\text{-}7)$$

where:

$[A]_0$ = initial concentration of A

$[A]$ = concentration of A at time t .

The logarithmic form of Equation 3-7 is:

$$\ln[A]=\ln[A]_0 - kt \ . \quad (3\text{-}8)$$

This implies that the first order rate constant, k, can be determined by plotting ln[A] versus time. The plot is a straight line, with the slope equal to "-*k*" and the intercept equal to "ln$[A]_0$". First order rate constants were calculated from the slope of ln[COD] over time elapsed since each injection using data from TSF-05A, TSF-05B, TAN-25, and TAN-31 (Table 3-8). Table 3-9 presents the estimated first order degradation rate constants for lactate after each of the different injections.

Table 3-8. First order chemical oxygen demand degradation rate constants during different injection strategies.

Well	Oct. 2002 4X 3%	Jan. 2003 4X 3%	Feb. 2003 4X 3%	Jul. 2003 1X 6%	Sept. 2003 1X 6%
TSF-05A	0.11	0.12	0.12	0.17	0.17
TSF-05B	0.10	0.12	0.11	0.15	0.17
TAN-25	0.10	0.10	0.12	0.15	0.13
TAN-31	0.18	N/A	0.15	N/A	0.15

Table 3-9. First order lactate degradation rate constants during different injection strategies.

Well	Oct. 2002 4X 3%	Jan. 2003 4X 3%	Feb. 2003 4X 3%	Jul. 2003 1X 6%	Sept. 2003 1X 6%
TSF-05A	0.33	0.37	0.30	0.47	0.36
TSF-05B	0.35	0.40	0.30	0.51	0.54
TAN-25	0.19	0.25	0.23	0.47	0.27
TAN-31	0.31	0.26	0.27	N/A	0.02

The rate constants calculated using COD values estimate the degradation rate for the combined electron donor within the system, providing a more general interpretation of electron donor utilization. Therefore, the estimated rates are less than the lactate rates but generally greater than either the propionate or acetate values (data not shown). The rate constants calculated using COD data for TAN-25, TSF-05A, and TSF-05B were generally lower following the 4X 3% injections (0.10-0.12) and higher following the 1X 6% injections (0.13-0.17; see Table 3-8). TAN-31 was an exception, however, where the calculated rate constants during the 4X 3% injection (0.18 and 0.15) were slightly higher than those for the other source area wells and did not increase during the 1X 6% injections, as did the other wells. This is likely due to the fact that TAN-31 is 50 ft crossgradient and exhibited much higher COD concentrations during the 4X 3% injections (3,000 mg/L) than during the 1X 6% injections (800 mg/L).

The lactate first order degradation rate constants that were calculated for the different injection strategies are shown in Table 3-9. In general, lactate and COD correlated well, with the highest degradation rate values observed during the 1X 6% injections, as compared with the 4X 3% injections for all source area wells except TAN-31. At TAN-31, higher degradation rates were observed during the 4X 3% injections, which is consistent with the fact that only during these injections did significant lactate reach TAN-31 to obtain reliable rate calculations. The degradation rate constant calculated after the September 2003 1X 6% lactate injection (0.02) is not reliable because lactate concentrations were very low (<5.5 mg/L).

Table 3-10 presents the molar propionate:acetate ratios observed for wells TAN-25, TAN-31, TSF-05A, and TSF-05B six to eight days after the different injections occurred. Overall, the values ranged from 0.31 to 1.11. It is important to note that the ratio for TAN-31 was much higher than those for TAN-25, TSF-05A, and TSF-05B. The propionate:acetate in all of the source area wells was the highest following the October 2002 4X 3% injection and lowest following the September 2003 1X 6% injection. A dramatic decline in the ratio was also observed at TSF-05A, TSF-05B, and TAN-25 after switching the injection strategy to the 1X 6% injection in July 2003. This can be correlated to increased lactate degradation rates after the 1X 6% injections began.

Table 3-10. Propionate:acetate ratios for source wells after different injection strategies.

Well	Oct. 2002 4X 3%	Jan. 2003 4X 3%	Feb. 2003 4X 3%	Jul. 2003 1X 6%	Sept. 2003 1X 6%
TSF-05A	1.04	0.74	0.69	0.63	0.57
TSF-05B	0.94	0.55	0.54	0.37	0.31
TAN-25	0.82	0.68	0.69	0.49	0.34
TAN-31	1.11	0.95	1.03	1.05	0.72

3.1.4 Redox Conditions

In order for ARD of chloroethenes to proceed to completion at meaningful rates, the process must be energetically favorable. Therefore, the complete transformation of TCE to ethene by ARD requires the absence of competing electron acceptors like oxygen, nitrate, ferric iron, manganese (IV), and sulfate. Anaerobic reductive dechlorination of TCE to cis-DCE requires redox conditions to favor iron and sulfate reduction, but complete dechlorination to ethene requires redox conditions to favor methane production. At TAN, the most efficient ARD observed has been correlated to the onset of significant methanogenesis. Methanogenic conditions are indicated by the absence of sulfate (and other acceptors), the presence of ferrous iron, and the presence of methane. Thus, the presence of ferrous iron, sulfate, and methane were used to determine whether changes in redox conditions associated with the presence/absence of electron donor could be observed throughout the treatment cell. Redox parameter data throughout the system are presented in Figures 3-12 through 3-23.

3.1.4.1 Source Area and Deep Wells. The source area and deep wells continued to be methanogenic throughout the reporting period; sulfate was completely absent, ferrous iron was elevated, and significant methane production was observed as concentrations approached the solubility limits in most wells (Figures 3-12 through 3-23). Decreases in methane concentrations below 5,000 µg/L immediately following injections were likely a result of dilution by the electron donor solution.

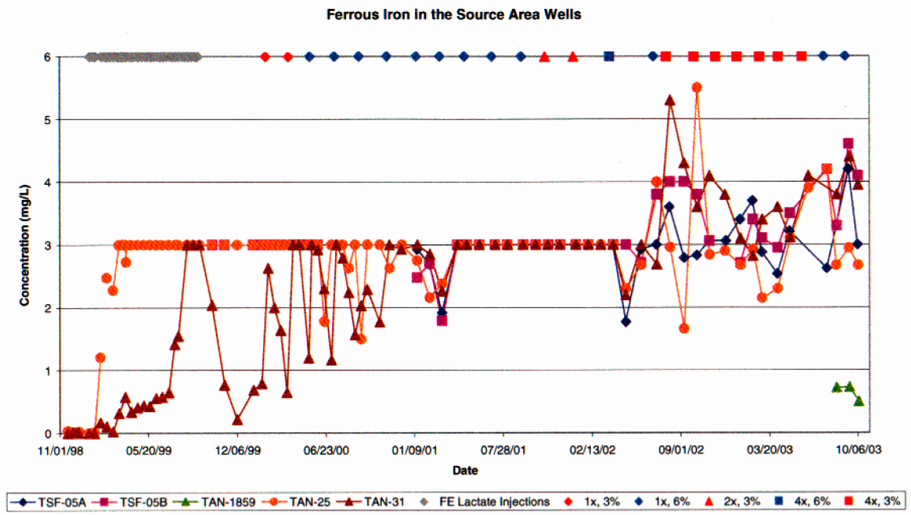

Figure 3-12. Ferrous iron at the source area wells.

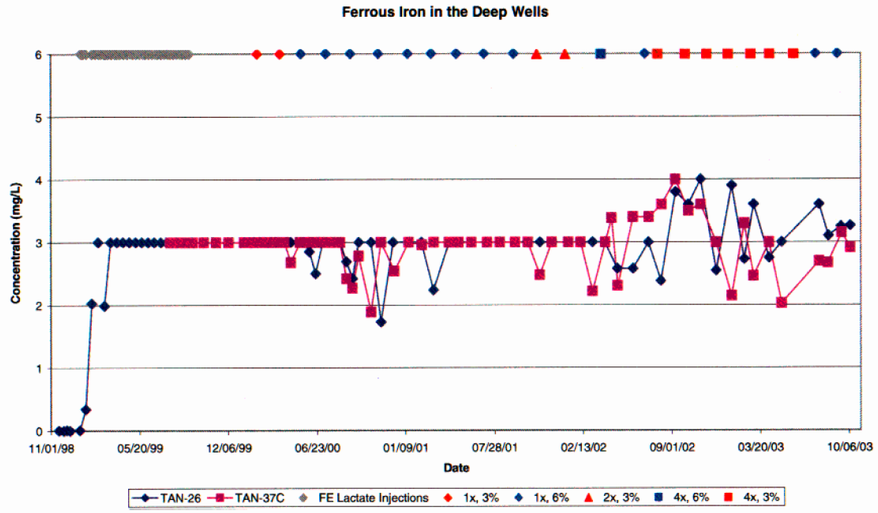

Figure 3-13. Ferrous iron at the deep wells.

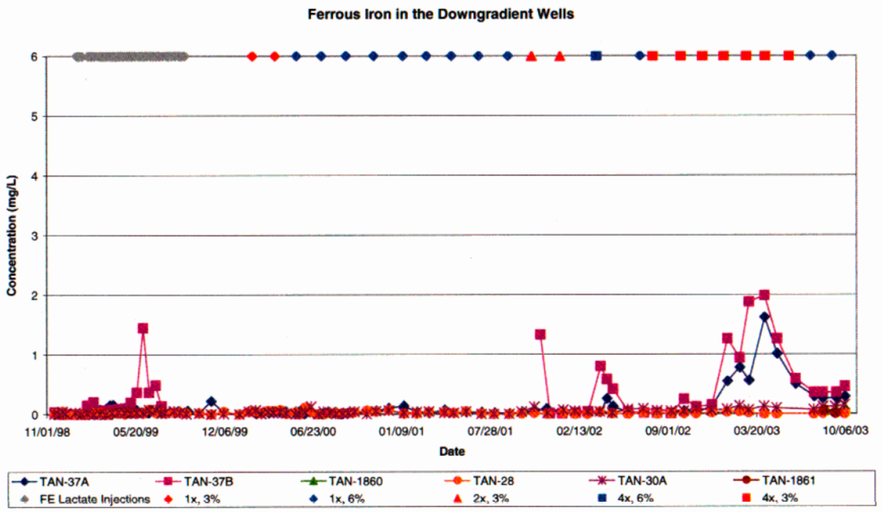

Figure 3-14. Ferrous iron at the downgradient wells.

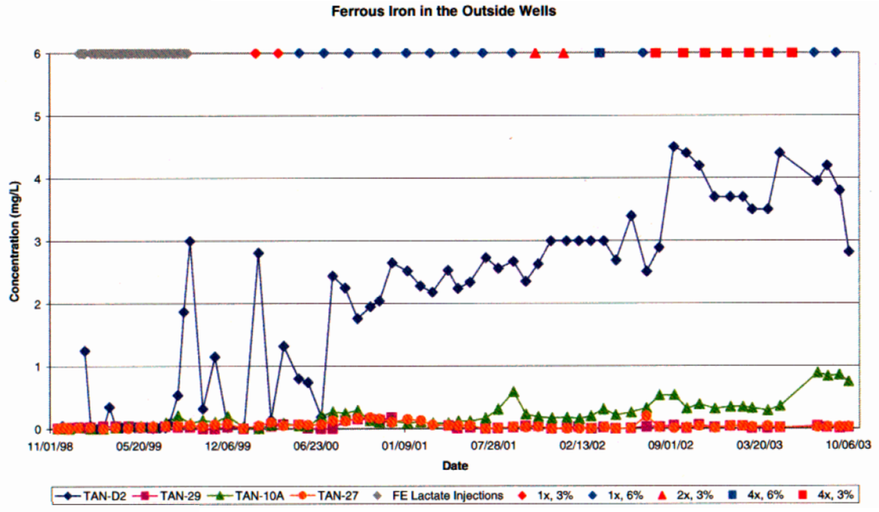

Figure 3-15. Ferrous iron at the outside wells.

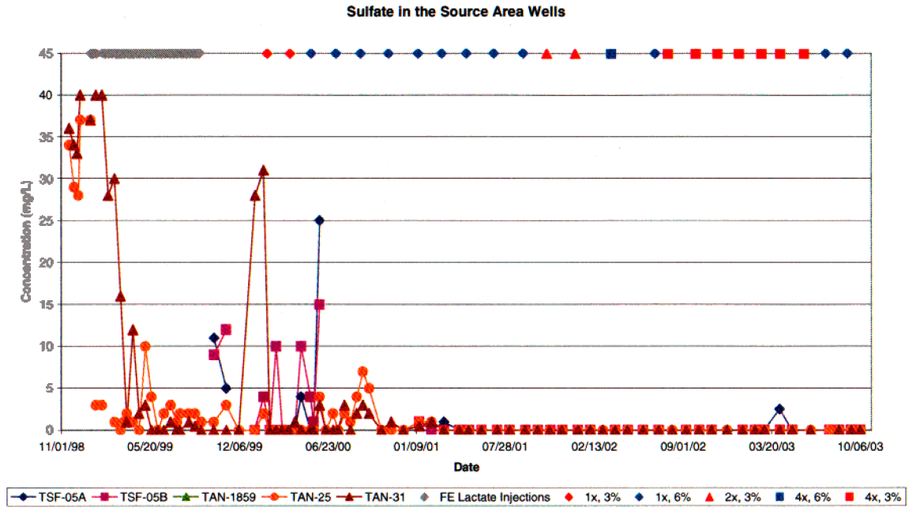

Figure 3-16. Sulfate at the source area wells.

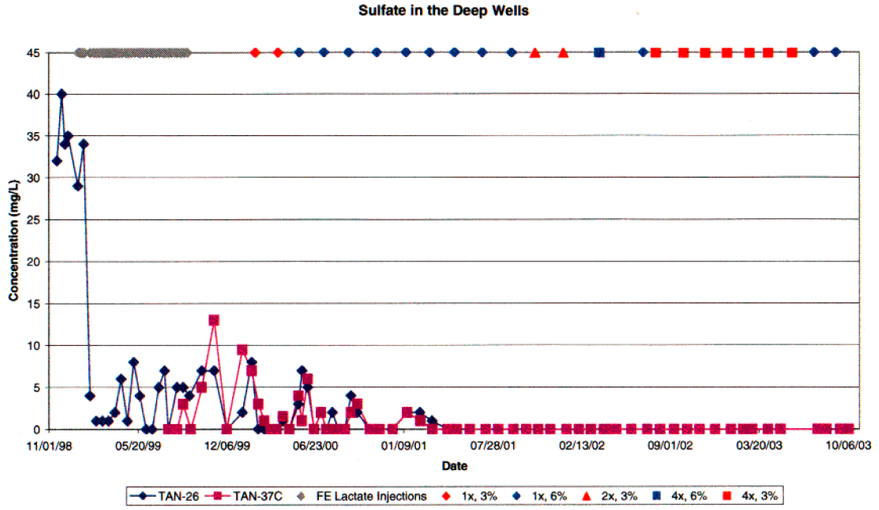

Figure 3-17. Sulfate at the deep wells.

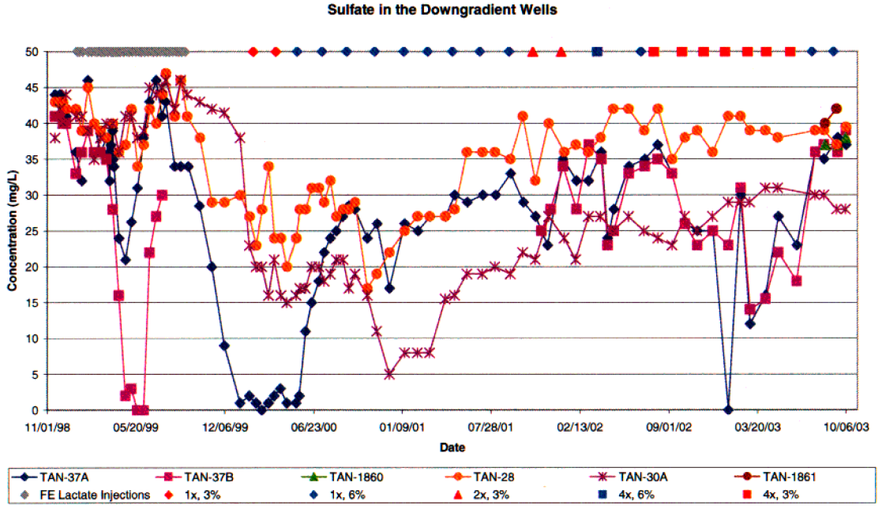

Figure 3-18. Sulfate at the downgradient wells.

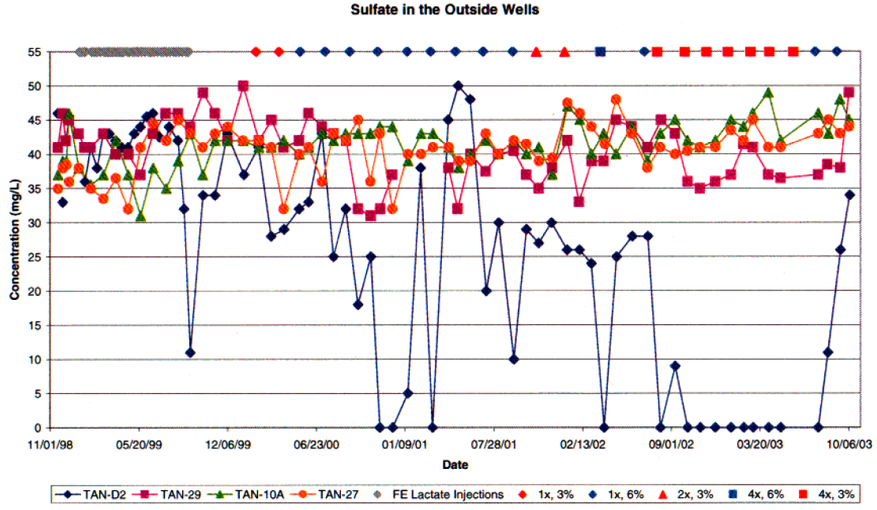

Figure 3-19. Sulfate at the outside wells.

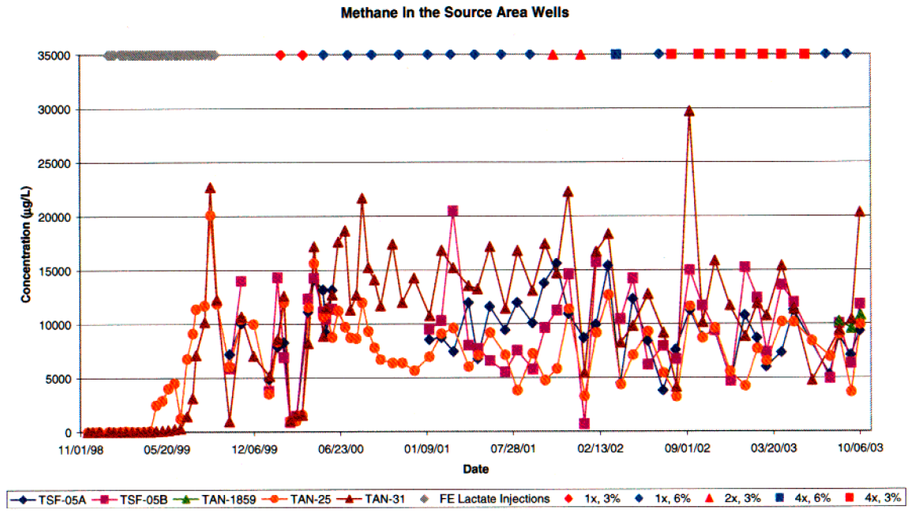

Figure 3-20. Methane at the source area wells.

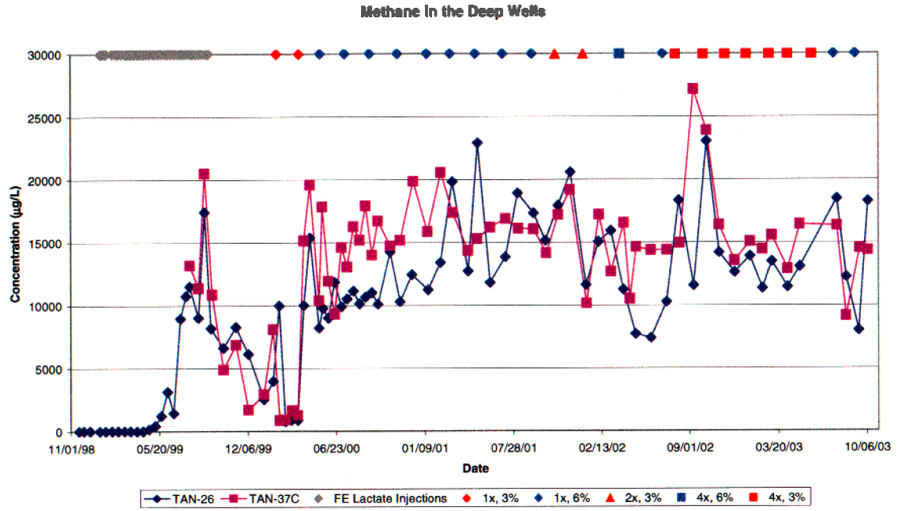

Figure 3-21. Methane at the deep wells.

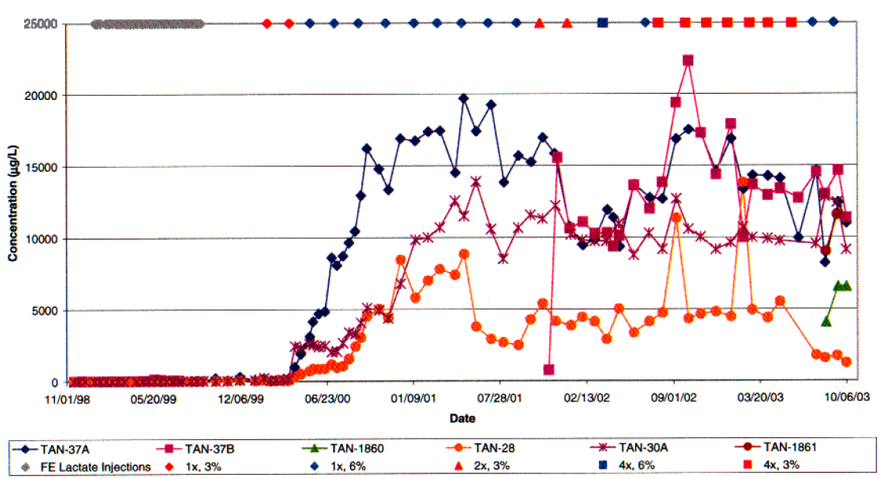

Figure 3-22. Methane at the downgradient wells.

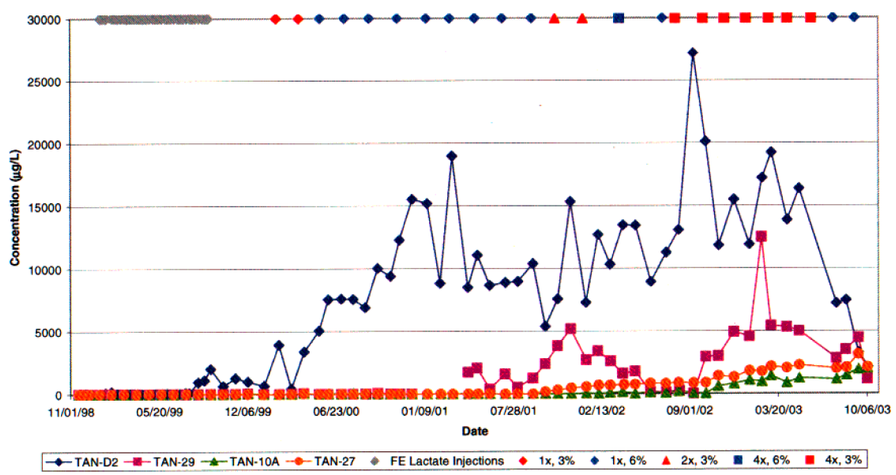

Figure 3-23. Methane at the outside wells.

3.1.4.2 Downgradient Wells. Methane was present at all of the ISB downgradient monitoring locations. Methane at TAN-37A ranged from approximately 8,000 to 18,000 μg/L over the reporting period. Methane at TAN-37B ranged from approximately 10,000 to 18,000 μg/L over the reporting period. Methane at TAN-28 fluctuated in response to the different injections. Overall, during the 4X 3% injections methane was typically in the vicinity of 4,000 μg/L, with the exception of the data collected on February 10, 2003, where methane was nearly 14,000 μg/L. With the implementation of the 1X 6% injection strategy, the methane concentration at TAN-28 dropped substantially with observed concentrations of approximately 2,000 μg/L. TAN-30A methane concentrations have remained steady at approximately 10,000 mg/L. The presence of methane at the downgradient wells can be attributed to transport from the source area rather than to active methanogenesis, as evidenced by the lack of ferrous iron and elevated levels of sulfate.

Unlike the source area wells where changes in redox conditions could be correlated to the presence of electron donor, the downgradient wells often saw changes in redox without the presence of electron donor. This is likely due to transport of reducing water from upgradient locations. For instance, at TAN 37A and TAN-37B, redox conditions were initially impacted in response to the 4X 3% injections. For example, ferrous iron increased at TAN-37A from 0.05 mg/L on October 8, 2002, to a maximum concentration of 1.62 mg/L on April 8, 2003. Sulfate at this location also dropped to 0 mg/L on January 14, 2003. However, these changes were temporary. Approximately 8 months after the start of the 4X 3% injections, redox conditions reverted to less reducing conditions at the downgradient locations.

3.1.4.3 Outside Wells. As described in Section 3.1.1, electron donor was not distributed to most outside well locations. TAN-D2 is the only outside well where redox conditions have been impacted by ISB electron donor injections. Although little electron donor was distributed to TAN-D2 during the reporting period, electron donor has been seen at this location in the past (INEEL 2002a). Methane and ferrous iron have been observed in TAN-D2 since PDP-II, but the presence of significant sulfate (~30 mg/L) suggested that these constituents were transported to TAN-D2 as a result of electron donor injections at TSF-05. During the 4X 3% injections, however, sulfate concentrations were depleted to 0 mg/L and high concentrations of ferrous iron (>3 mg/L) and methane (>10,000 μg/L) were observed, which suggested electron donor was directly impacting the area near TAN-D2, although electron donor was not measured in significant concentrations. When the injection strategy was changed back to 1X 6%, sulfate rebounded at this location (by October 7, 2003, sulfate at TAN-D2 was 34 mg/L) and methane concentrations dropped to below 5,000 μg/L, which was the lowest concentration observed since before May of 2000. Ferrous iron concentrations, however, have remained high, which suggests that this location is currently under iron-reducing conditions.

3.1.5 Anaerobic Reductive Dechlorination

During this reporting period, the efficiency of the ARD reactions was assessed by examining changes in relative concentrations of TCE, cis-DCE, VC, and ethene. High concentrations of ethene relative to TCE, cis-DCE, and VC indicate that ARD reactions are operating efficiently. This period's groundwater monitoring results are reported in the subsequent sections in terms of source area wells, deep wells, downgradient wells, and outside wells. Figures 3-24 through 3-40 present the relative molar concentrations of the VOCs from the beginning of monitoring through the end of Interim Operations.

3.1.5.1 Source Wells. Anaerobic reductive dechlorination has continued in all source area wells throughout the reporting period. Ethene is the dominant compound at TSF-05A and TSF-05B. However, a change in cis-DCE concentrations at TAN-25 and TAN-31 was evident during this reporting period.

Historically, VOC concentrations in wells TAN-25 and TAN-31 remained at relatively low levels (less than 100 μg/L). During this reporting period, however, cis-DCE exhibited significant concentration

spikes in response to the 4X injections. For example, at TAN-25, cis-DCE concentrations peaked at 300 µg/L on January 14, 2003, which was about 100 µg/L greater than the highest concentration observed during the previous reporting period. By February 11, 2003, (4 weeks later) concentrations at this location had only declined to 165 µg/L. Although cis-DCE concentrations did eventually return to typical levels, the average concentration during the 4X 3% injections were substantially greater than what had been previously observed. Concentrations at TAN-31 showed similar trends in response to the start of the 4X 3% injections. The magnitude of the cis-DCE concentration spikes in TAN-25 and TAN-31 began to decline following the implementation of the 1X 6% injection strategy and as of the end of the reporting period, were near the pre-4X 3% injection conditions. The cis-DCE fluxuations in response to injections are discussed in Section 4.

Trans-DCE continued to be a relatively recalcitrant compound at each of the source area wells, although concentrations appear to be declining. The chlorine number at each of the source area wells was greatest (2.5 to 3.0) at the beginning of the ISB treatment process because of the predominance of TCE and DCE. In areas impacted by electron donor injections, the chlorine number declined to between 1.5 and 2 but remains relatively steady now because the dominant compounds are trans-DCE and ethene (Figures 3-24 through 3-40).

3.1.5.2 Deep Wells. Volatile organic compounds at TAN-26, with the exception of trans-DCE, have been near or below MCLs since January 2000 (Figure 3-29). Since the beginning of the field evaluation, trans-DCE has persisted with concentrations near or below MCLs (between 80 to 130 µg/L) at this well. For well TAN-37C, TCE and cis-DCE were below MCLs (Figure 3-30). Vinyl chloride was below detection limits during the first 6 months of the reporting period, with the exception of one measurement of 25 µg/L in January 2003. During the second half of the reporting period, however, VC concentrations increased at this location. During May through July 2003, VC ranged from 12 to 16 µg/L; during August through October 2003, VC ranged from 32 to 40 µg/L. Although the initial increase occurred during the 4X injections, the highest concentrations were measured from August through October after the onset of the 1X 6% injection strategy. Trichloroethene and cis-DCE concentrations at this location also increased after the onset of the 1X 6% injections. July through October TCE concentrations ranged from 13 to 14 µg/L. July through October cis-DCE concentrations ranged from 10 to 26 µg/L. As of the end of the reporting period, VOC concentrations remained above MCLs at this location.

3.1.5.3 Downgradient Wells. Although electron donor was not distributed to the downgradient locations, changes in VOC concentrations could be correlated to the 4X 3% injection strategy, particularly at TAN-37A and TAN-37B (Figures 3-31 and 3-32). Over the past 3 years, the TCE concentrations at these locations have been around 200 to 400 µg/L. After 4X 3% injections began (July 2002), TCE concentrations steadily declined at both of these sampling locations. Ultimately, TCE concentration at TAN-37A reached 39 µg/L on April 8, 2003, which was the lowest concentration ever observed at this location. A similar trend was observed at TAN-37B, with the lowest TCE concentration observed at 30 µg/L on March 4, 2003. This drop in TCE was correlated to increases in cis-DCE concentrations, which reached 69 µg/L in samples collected April 8, 2003, in TAN-37A and 96 µg/L in samples collected March 4, 2003, in TAN-37B. These changes in VOC concentrations correlated to redox changes in TAN-37A and TAN-37B, as described in Section 3.1.4.2. (One sample collected at TAN-37B on November 5, 2002, indicated that TCE concentrations were <10 µg/L, but off-Site split data, as well as comparisons to the concentration trend, indicate that this point was an anomaly.) After approximately 8 months of 4X 3% injections, however, TCE concentrations at TAN-37A began to rebound. TCE concentrations had reached 174 µg/L at TAN-37A and 130 µg/L at TAN-37B by October 7, 2003.

Volatile organic compound concentrations at TAN-28 and TAN-30A remained fairly constant with the TCE concentration at TAN-28 ranging from 900 to 1,300 μg/L (Figures 3-34 and 3-35). TAN 28 TCE data from May 5, 2003, and September 15, 2003, were substantially lower than the other TCE points. When compared to the overall trend of TCE concentration, it can be concluded that these two points were outliers to the general trend and should not be taken as indicative of conditions at these locations. In addition, off-Site split data from May 5, 2003, showed TCE to have a concentration of 1,300 μg/L, which is similar to other TCE data from this location. Cis-DCE concentrations have remained steady at TAN-28, typically in the range of 100 to 150 μg/L). Trans-DCE concentrations at this location also remained steady for most of the reporting period, with concentrations at approximately 160 μg/L. However, samples collected after July 28, 2003, consistently show lower trans-DCE concentrations at 76.4 and 86.4 μg/L. TCE concentrations at TAN-30A remained steady at approximately 80 μg/L. During most of the reporting period, trans-DCE concentrations at TAN-30A remained steady (44 to 51 μg/L); samples collected after July 28, 2003, however, were consistently higher (81.6 to 96.9 μg/L). The period before the July 28, 2003, sampling round correlates to the period when 4X 3% injections were occurring; the period after that sampling round is during 1X 6% injections.

3.1.5.4 Outside Wells. Volatile organic compound concentrations in outside wells have shown little change during the reporting period, with the exception of decreasing concentrations observed in TAN-D2 (Figure 3-37). All VOCs at TAN-10A were near or below MCLs (Figure 3-39). Trichloroethene concentrations at TAN-27 (Figure 3-40) were generally steady with values at approximately 40 μg/L (3.04×10^{-7} mol/L); one exception was the sample collected on October 6, 2003, which was nondetect. Sporadic detections of tetrachloroethene (PCE) have been observed at this location; however, these appeared to be isolated spikes rather than representative of an overall increasing trend. All other VOCs at this location were below the method detect limit for all samples collected during the reporting period. Volatile organic compound concentrations at TAN-29 have remained fairly constant throughout the reporting period (Figure 3-38). Trichloroethene concentrations ranged from highs of approximately 800 μg/L, from samples taken October 7, 2002, January 13, 2003, and July 28, 2003, after electron donor injections, to lows of 600 μg/L, from samples taken December 9, 2002, May 5, 2003, and October 6, 2003, approximately 4 weeks after electron donor injections. The increasing and decreasing trends associated with electron donor injection occurred during both the 4X 3% and 1X 6% injections. Cis-DCE (approximately 130 μg/L) and trans-DCE (approximately 100 μg/L) concentrations were generally constant throughout the reporting period, with the exceptions of the last data point collected 10/6/03 in which trans-DCE dropped to 18.3 μg/L and cis-DCE dropped to 67.6 μg/L. For well TAN-D2, three samples collected during the reporting period had TCE concentrations above 10 μg/L, and one sample had a VC concentration at 15.3 μg/L. All other samples had VOC concentrations below MCLs, with the exception of trans-DCE. Trans-DCE concentrations at TAN-D2 initially ranged from 112.2 to 141.3 μg/L, but samples collected after July 28, 2003, show a decreasing trend in concentrations to 19.7 μg/L for the sample collected October 7, 2003. This declining trend correlates with the switch of the injection strategy from a 4X 3% to a 1X 6%, with the increase in redox conditions from methanogenic to sulfate-reducing and a decline in COD reaching this location.

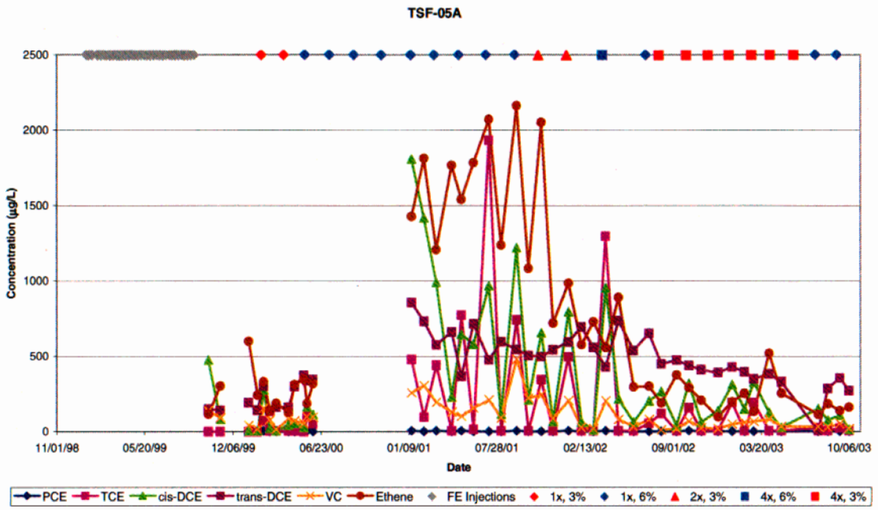

Figure 3-24. Anaerobic reductive dechlorination at TSF-05A.

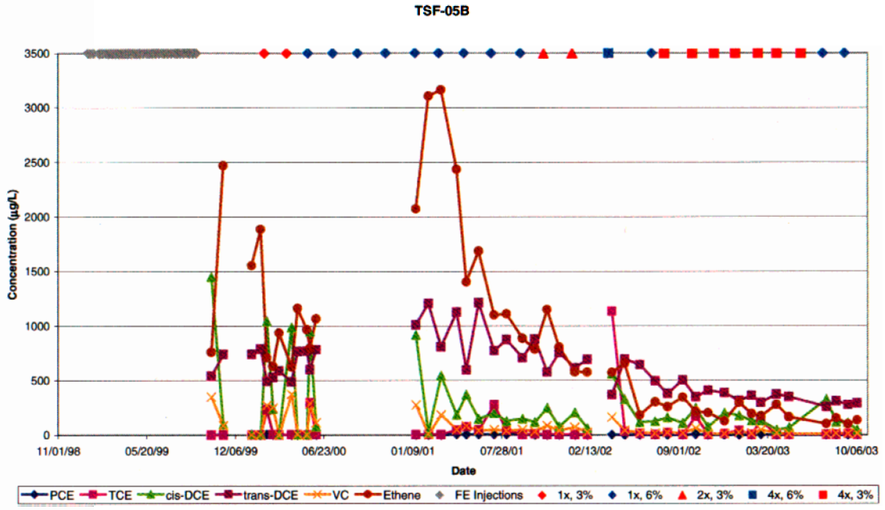

Figure 3-25. Anaerobic reductive dechlorination at TSF-05B.

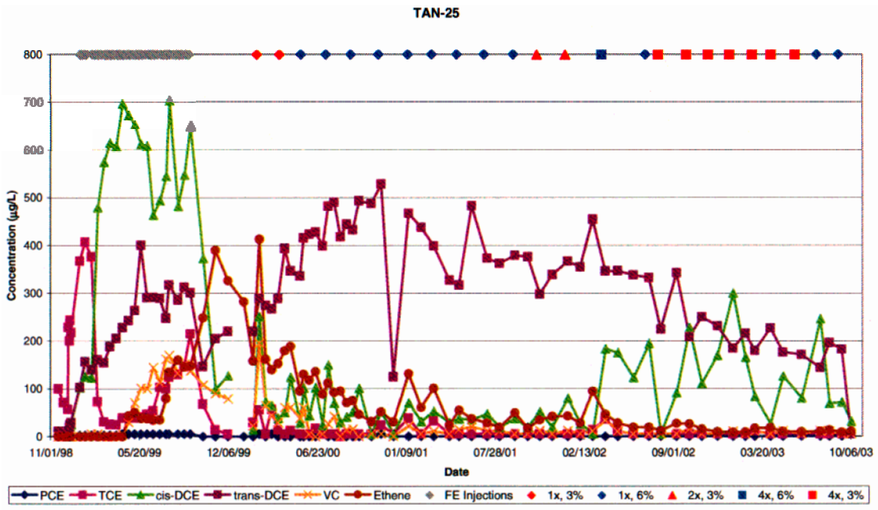

Figure 3-26. Anaerobic reductive dechlorination at TAN-25.

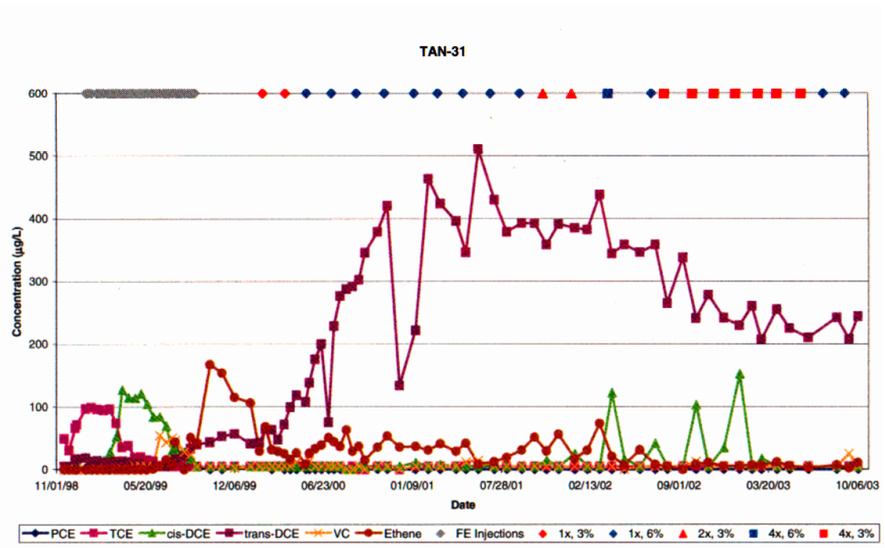

Figure 3-27. Anaerobic reductive dechlorination at TAN-31.

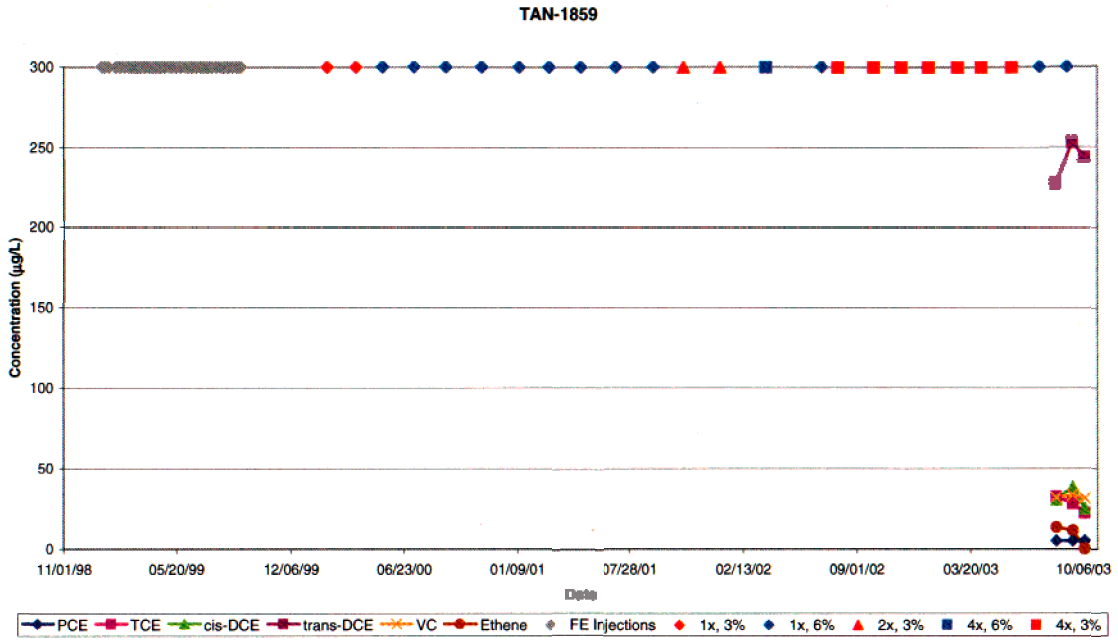

Figure 3-28. Anaerobic reductive dechlorination at TAN-1859.

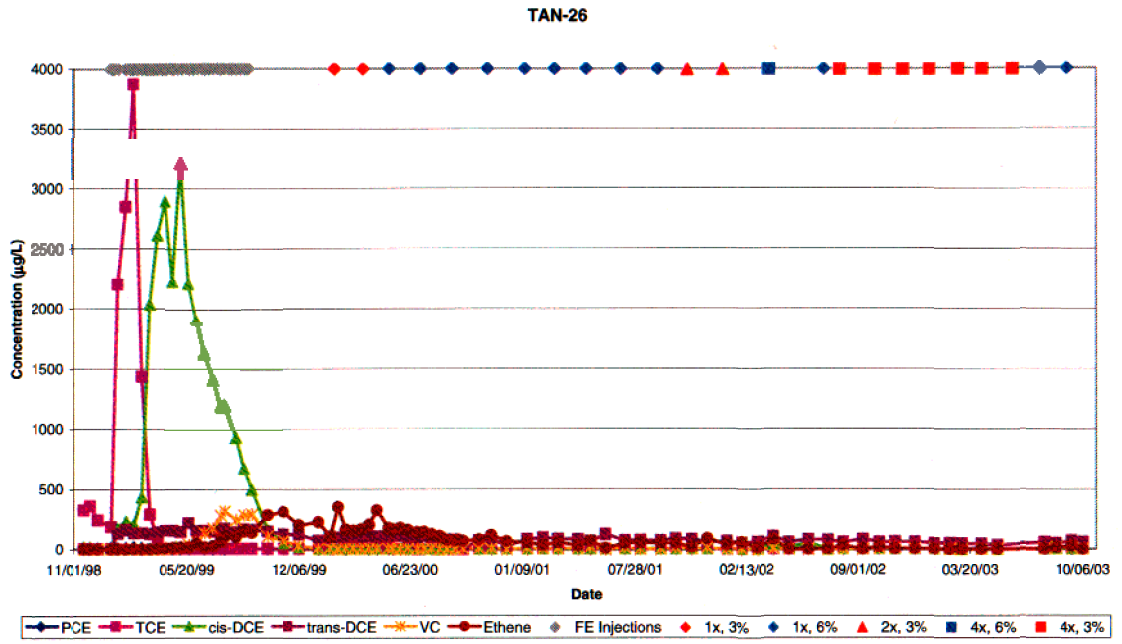

Figure 3-29. Anaerobic reductive dechlorination at TAN-26.

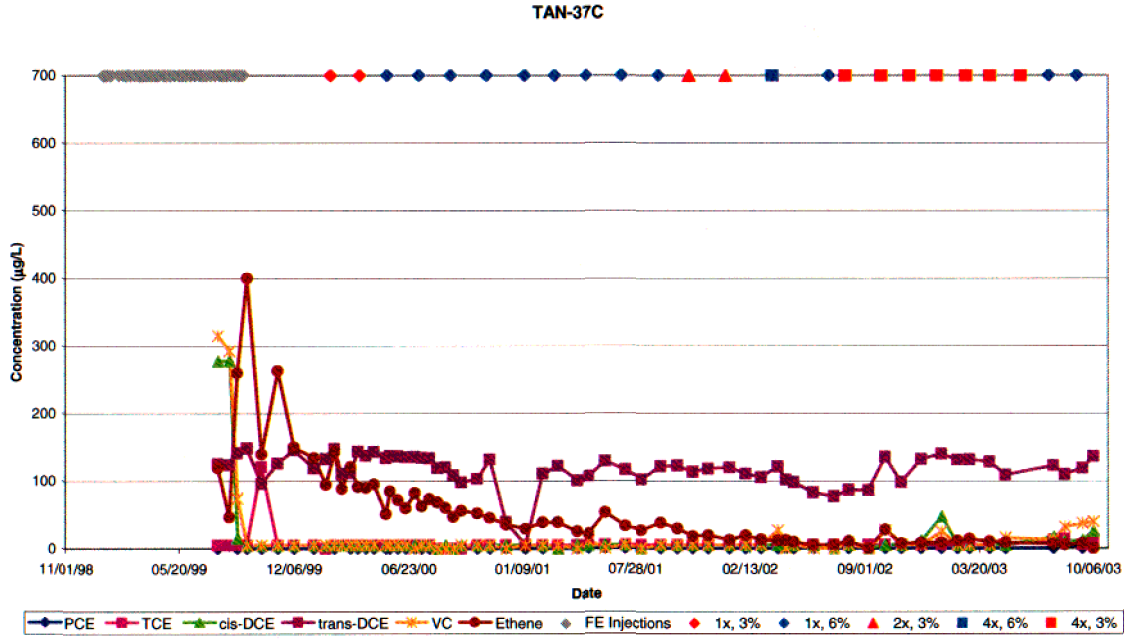

Figure 3-30. Anaerobic reductive dechlorination at TAN-37C.

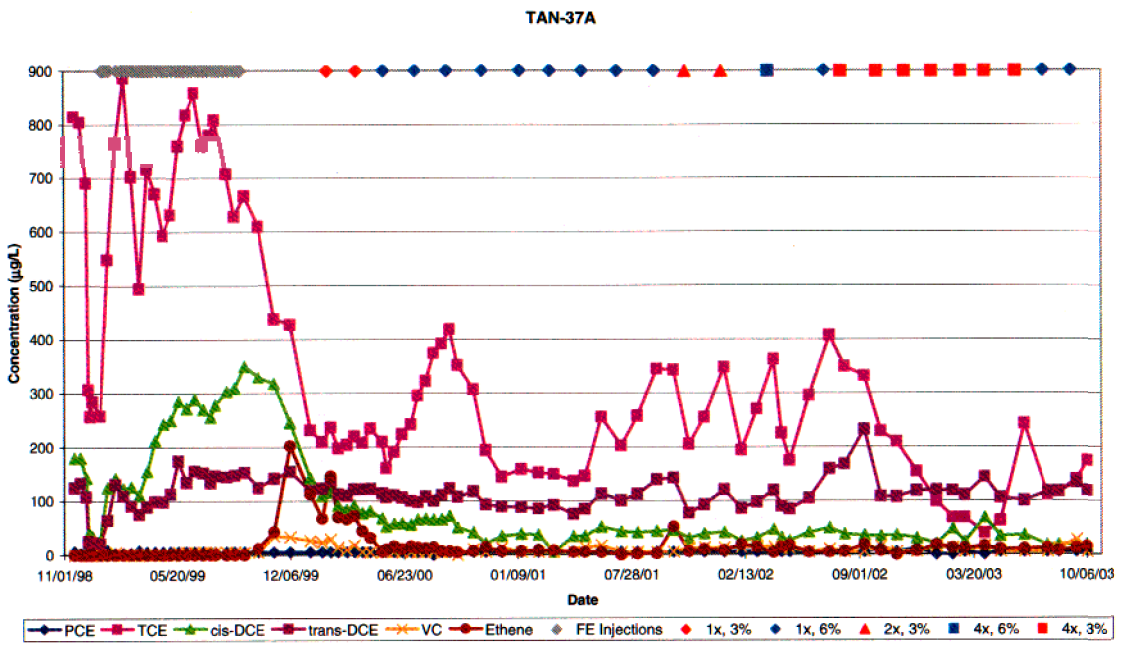

Figure 3-31. Anaerobic reductive dechlorination at TAN-37A

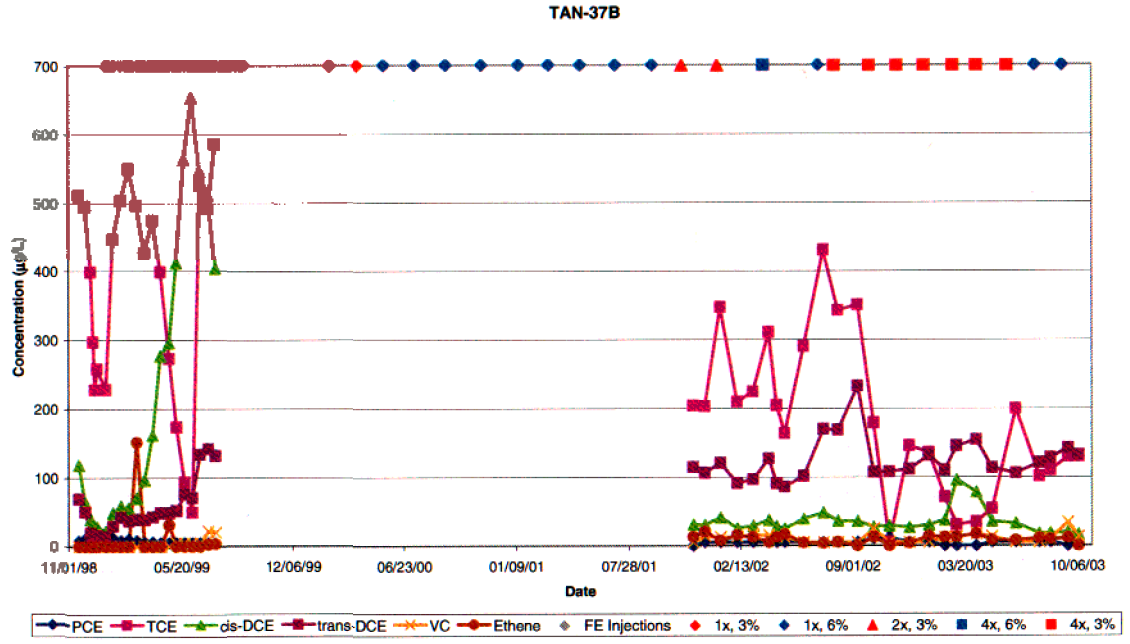

Figure 3-32. Anaerobic reductive dechlorination at TAN-37B.

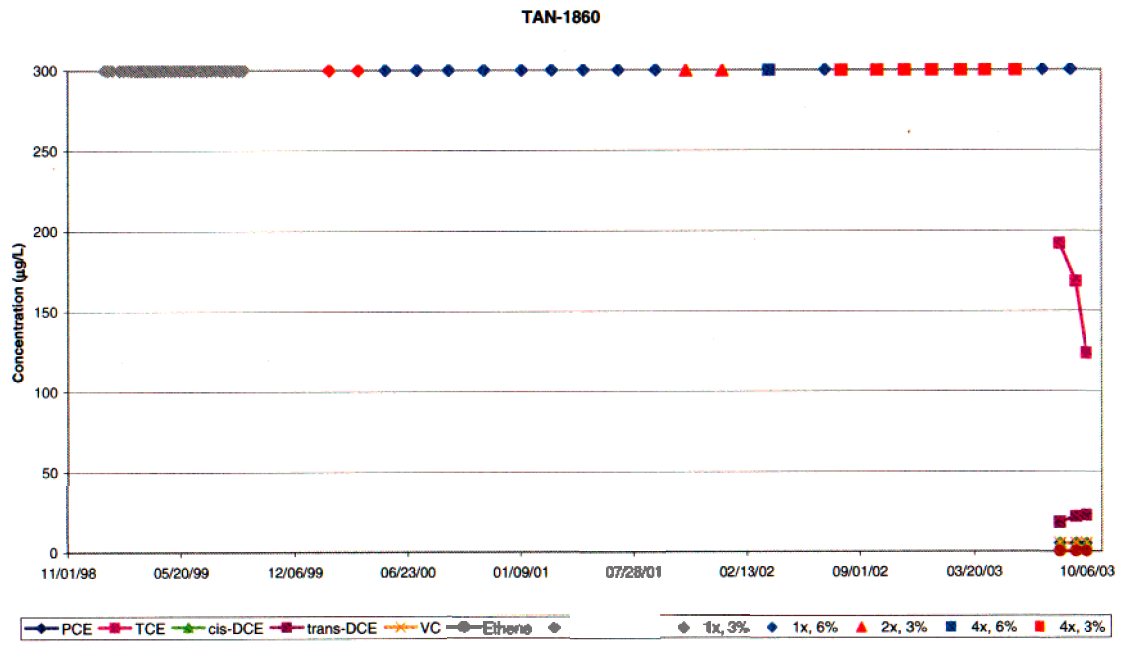

Figure 3-33. Anaerobic reductive dechlorination at TAN-1860.

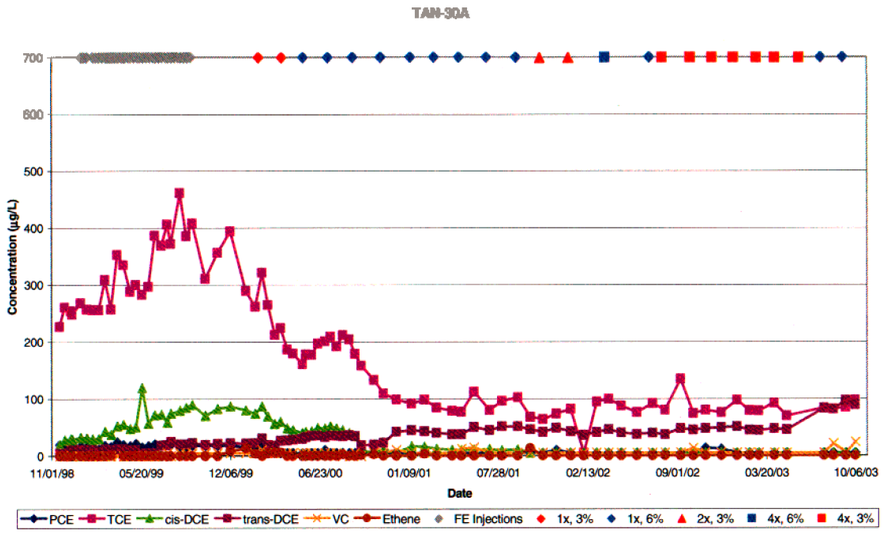

Figure 3-34. Anaerobic reductive dechlorination at TAN-30A.

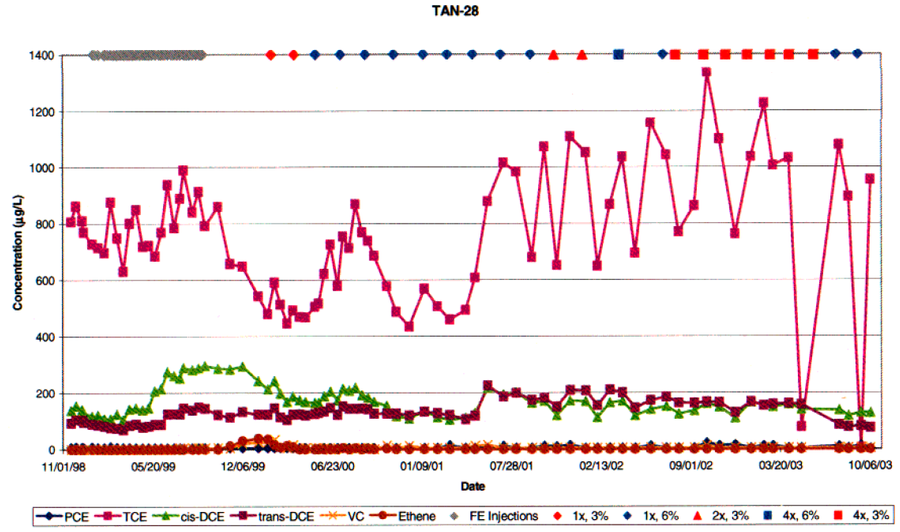

Figure 3-35. Anaerobic reductive dechlorination at TAN-28.

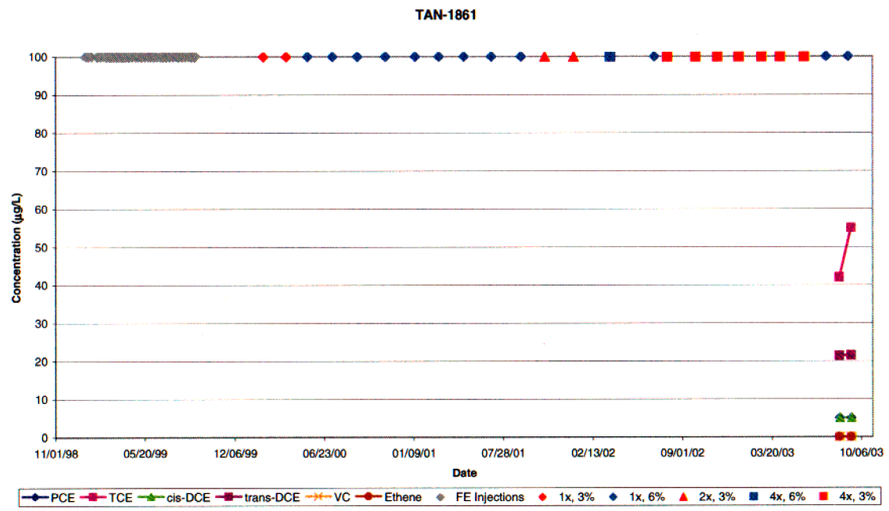

Figure 3-36. Anaerobic reductive dechlorination at TAN-1861.

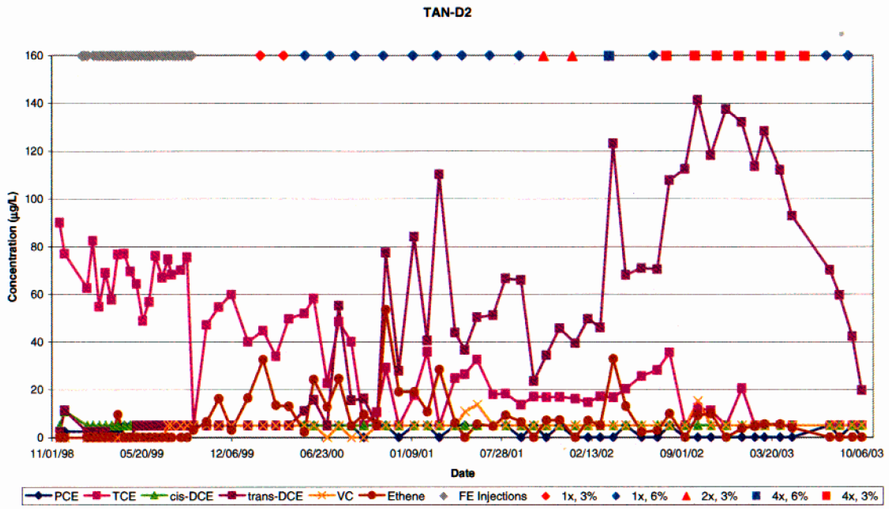

Figure 3-37. Anaerobic reductive dechlorination at TAN-D2.

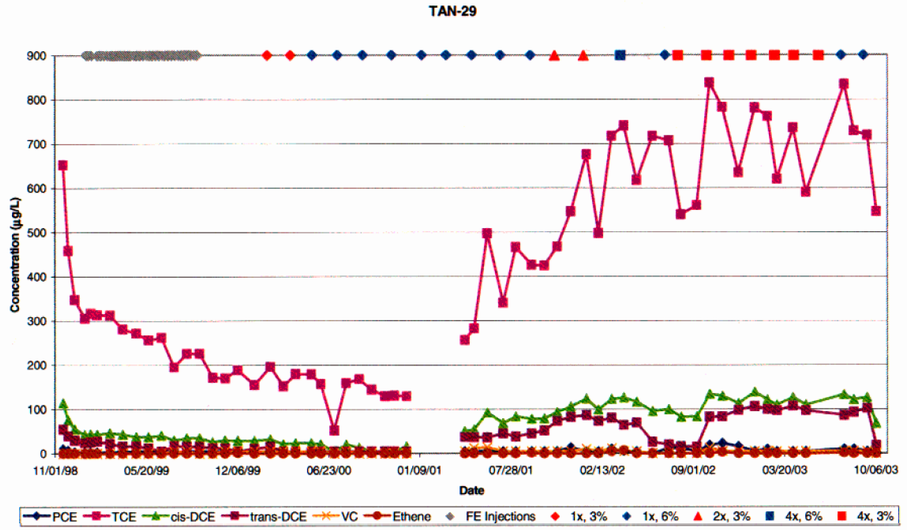

Figure 3-38. Anaerobic reductive dechlorination at TAN-29.

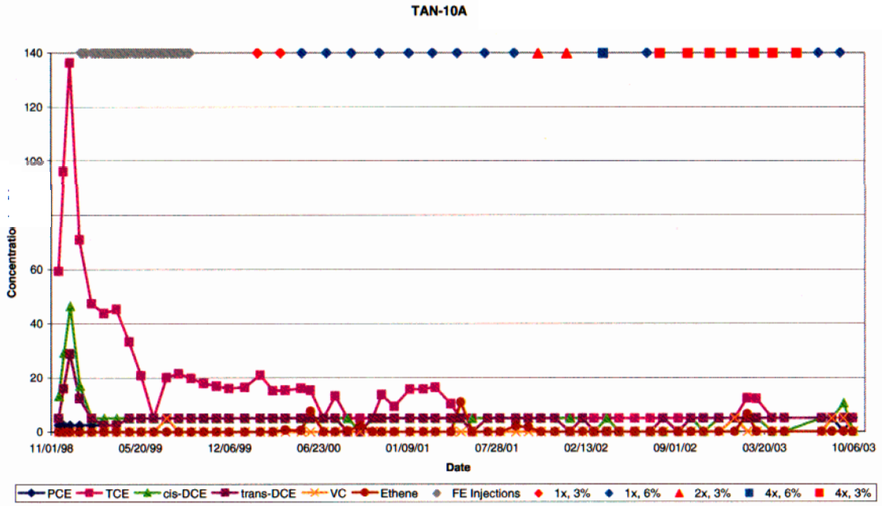

Figure 3-39. Anaerobic reductive dechlorination at TAN-10A.

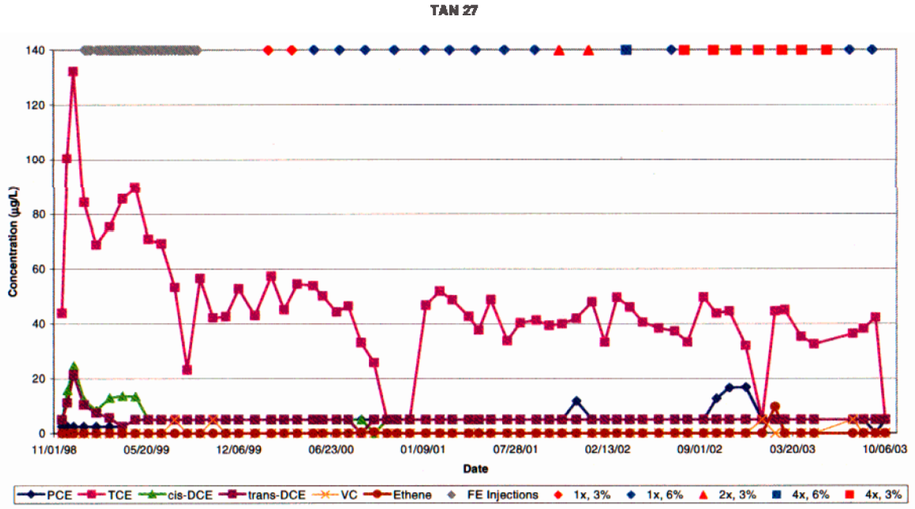

Figure 3-40. Anaerobic reductive dechlorination at TAN-27.